

The Atomic Order of the Pnictogen and Chalcogen Atoms in Equiatomic Ternary Compounds $TPnCh$ ($T = Ni, Pd; Pn = P, As, Sb; Ch = S, Se, Te$)

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The crystal structures of the compounds NiAsS, NiSbS, PdAsS, PdAsSe, PdSbSe, and PdSbTe were refined from single-crystal X-ray diffractometer data. In these cubic compounds the pnictogen and chalcogen atoms show an ordered distribution corresponding to the ullmannite (NiSbS) type structure (space group $P2_13$, $Z = 4$). By analogy this can be assumed for NiPS and NiAsSe, although for these compounds the structure refinements did not make it possible to distinguish between a disordered distribution of the pnictogen and chalcogen atoms (corresponding to the pyrite structure) or an ordered distribution (corresponding to ullmannite or cobaltite). All atomic positions are fully occupied within the error limits of $\pm 2\%$. A refinement from X-ray powder data established the ullmannite structure also for NiSbSe. The PdPS type structure of PdPSe was refined from single-crystal data. No equiatomic ternary compounds were observed in the ternary systems Ni–P–Se, Ni–P–Te, Ni–As–Te, Ni–Sb–Te, Pd–P–Te, and Pd–As–Te. A refinement from single-crystal data showed $Ni_{0.766(5)}Sb_{0.50(3)}Te_{0.50(3)}$ to crystallize with a defect-NiAs type structure. Extended solid solutions were observed for the pseudobinary system NiP_2 – $NiSe_2$, where a slowly cooled equiatomic sample contained $NiP_{1.86(4)}Se_{0.14(4)}$ and $NiP_{0.24(4)}Se_{1.76(4)}$ as limiting compositions, as shown by structure refinements from X-ray powder data. Chemical bonding in these compounds is briefly discussed. © 2001 Academic Press

INTRODUCTION

The ternary compounds NiPS, NiAsS, NiSbS, NiAsSe, NiSbSe, PdAsS, PdSbS, PdAsSe, PdSbSe, and PdSbTe have been reported from powder data to crystallize with the pseudocubic cobaltite (CoAsS), or with pyrite (FeS₂), or with a cubic pyrite-related (for example, ullmannite) type structure (1–5). The X-ray powder patterns of these structures are very similar and it is difficult to establish the atomic order (or disorder) of the pnictogen and chalcogen atoms in these compounds from powder data. The mineral with the ideal composition NiSbS (ullmannite) seems to be the only compound for which a reliable structure has been

established from single-crystal (film) data (6). An orthorhombic ordered structure has been found for PdPS and PdPSe (7, 8). No structural information is available for the other 6 of the 18 possible combinations of the compositions $TPnCh$ ($T = Ni, Pd; Pn = P, As, Sb; Ch = S, Se, Te$) with one exception: the pseudobinary solid solution of the NiAs type $NiSb_{1-x}Te_x$ (9). The present investigation has been undertaken (a) to find out whether any of the missing compounds could be prepared, and (b) to unambiguously establish the crystal structure of the previously reported compounds.

PREPARATION AND LATTICE CONSTANTS

The ternary compounds were prepared by reaction of powders of the binary transition metal chalcogenides with the respective pnictogen component in evacuated sealed silica tubes. Starting materials for the preparation of the binary chalcogenides were powders of elemental nickel (Ventron, 99.9%), palladium (Chempur, >99.9%), sulfur (Merck, >99%), selenium (Fluka, >99.9%), and tellurium (Merck, >99%). The silica tubes were heated to ca. 1000°C under vacuum to evaporate any water. They were then flushed with argon, filled with the sample (the ratio transition metal:chalcogen was always 1:1), evacuated, sealed, placed in a cold furnace, heated to 450°C at a rate of 50°C/h, annealed at that temperature for 1 day, followed by heating to 800°C at 10°C/h, and kept at that temperature for 3 days. Finally the samples were quenched in cold water. The products were crushed to powders, thoroughly mixed with the elemental pnictogen to an overall atomic ratio of $T:Pn:Ch = 1:1:1$, and sealed again in evacuated silica tubes. The pnictogen components were semiconductor grade red phosphorus in compact form (Hoechst/Knapsack, “ultrapure”), arsenic (purified by fractional sublimation (10)), and antimony (Ventron, 99.5%). The samples were placed in a cold furnace and heated to 220°C at a rate of 50°C/h, kept at that temperature for 2 h, followed by

TABLE 1
Lattice Constants of the Equiatomic Ternary Transition Metal Pnictide Chalcogenides $TPnCh^a$

Compound	Space group	<i>a</i> (pm)	<i>b</i> (pm)	<i>c</i> (pm)	<i>V</i> (nm ³)	Reference
NiPS	$P2_13$	552.35(8)	—	—	0.16852(7)	This work
		554.4(3)	—	—	0.1704(3)	2
		554.9(2)	—	—	0.1709(2)	12
NiAsS	$P2_13$	568.83(6)	—	—	0.18405(5)	This work
		568.8(3)	—	—	0.1840(3)	2
		569.3	—	—	0.1845	3
		568.8	—	—	0.1840	5
NiSbS	$P2_13$	593.39(7)	—	—	0.20894(7)	This work
		593.3(3)	—	—	0.2088(3)	2
Ullmannite		588.1(2)	—	—	0.2034(2)	6
Ullmannite		588.6(1)	—	—	0.2039(1)	13
Ullmannite		592.18	—	—	0.2077	14
NiP _{1.86} Se _{0.14}	$Pa3$	547.9(1)	—	—	0.1644(1)	This work
NiP _{0.24} Se _{1.76}	$Pa3$	590.1(1)	—	—	0.2055(1)	This work
NiAsSe	$P2_13$	584.35(7)	—	—	0.19954(7)	This work
		584.5(3)	—	—	0.1997(3)	2
NiSbSe	$P2_13$	608.68(6)	—	—	0.22551(7)	This work
		609.0(3)	—	—	0.2259(3)	2
Ni _{0.77} Sb _{0.5} Te _{0.5}	$P6_3/mmc$	391.2(1)	—	519.4(1)	0.06884(5)	This work
PdPS	$Pbcn$	1330.6(1)	567.74(6)	569.3(1)	0.4301(1)	This work
		1330.4(4)	567.77(5)	569.32(5)	0.4301(1)	8
PdAsS	$P2_13$	594.76(4)	—	—	0.21039(4)	This work
		594.9(3)	—	—	0.2105(3)	2
PdSbS	$P2_13$	618.1(1)	—	—	0.2361(1)	This work
		618.5(3)	—	—	0.2366(3)	2
PdPSe	$Pbcn$	1358.8(2)	583.14(7)	585.90(7)	0.4643(2)	This work
		1356.9(4)	582.4(1)	585.6(1)	0.4628(2)	8
PdAsSe	$P2_13$	609.44(5)	—	—	0.22636(6)	This work
		609.2(3)	—	—	0.2261(3)	2
PdSbSe	$P2_13$	632.29(4)	—	—	0.25278(5)	This work
		632.3(3)	—	—	0.2528(3)	2
PdSbTe	$P2_13$	653.04(4)	—	—	0.27850(5)	This work
		653.3(3)	—	—	0.2788(3)	2

^aThe lattice constants of the compounds determined during the present investigation were obtained from Guinier powder data.

heating to 400°C at 50°C/h, annealed at that temperature for 24 h, heated further to 690°C at 10°C/h, and annealed at that temperature for 20 days. They were then slowly cooled to room temperature at a rate of 2°C/h.

The compact samples have metallic luster. They could easily be ground to fine, black powders, which were not sensitive to air. Energy-dispersive X-ray fluorescence analyses in a scanning electron microscope did not reveal any impurity elements heavier than sodium. The samples were characterized by their Guinier powder diagrams, recorded with $CuK\alpha_1$ radiation and α -quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. To assure correct indexing, the observed patterns were compared with the ones calculated using the program LAZY PULVERIX (11) and assuming positional parameters of structures with related compositions. The lattice constants were refined by least-squares fits. They are listed in Table 1 together with

those of previous publications. The unit cell volumes obtained during the present investigation are plotted in Fig. 1.

CRYSTAL STRUCTURE REFINEMENTS

The crystal structures of the 10 compounds NiPS, NiAsS, NiSbS, NiAsSe, Ni_{2-x}SbTe, PdAsS, PdPSe, PdAsSe, PdSbSe, and PdSbTe were determined from single-crystal data. For all of these compounds single crystals were isolated from the crushed samples. These were investigated on a Buerger precession camera to check their translational symmetry. For Ni_{2-x}SbTe a hexagonal cell corresponding to the well-known NiAs type structure was observed in agreement with the powder data. For PdPSe an orthorhombic cell was confirmed. It corresponds to that observed earlier (7, 8).

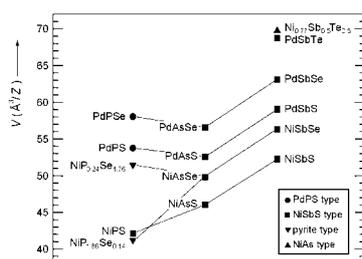
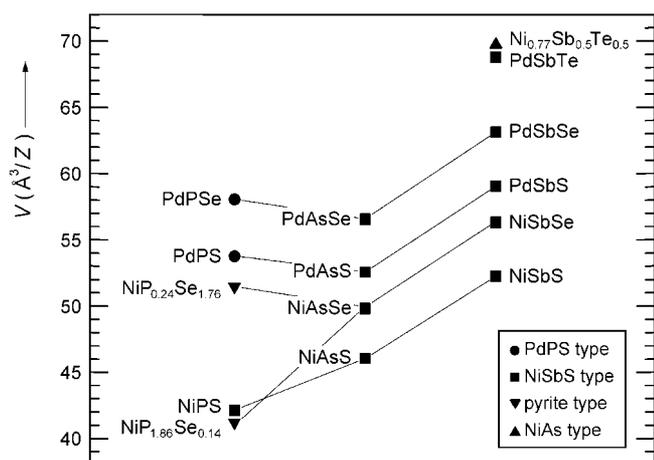


FIG. 1. Cell volumes per formula unit of the compounds $TPnCh$ ($T = \text{Ni, Pd}$; $Pn = \text{P, As, Sb}$; $Ch = \text{S, Se, Te}$), $\text{NiP}_{1.86}\text{Se}_{0.14}$, and $\text{NiP}_{0.24}\text{Se}_{1.76}$. The cell volume of the NiAs type compound $\text{Ni}_{0.766}\text{Sb}_{0.50}\text{Te}_{0.50}$ is plotted for the cell content $\text{Ni}_{1.53}\text{SbTe}$.

(i) NiPS , NiAsS , NiSbS , NiAsSe , PdAsS , PdAsSe , PdSbSe , and PdSbTe

For these eight compounds the X-ray powder patterns indicated a cubic cell as it is known for the pyrite (FeS_2) type structure. However, since the compounds contain two kinds of anionic atoms (pnictogens and chalcogens), one can expect an ordered arrangement, and at the outset it was not clear how these atoms might be ordered. The problem is illustrated in Fig. 2. One possibility is the atomic order, as it is known for the ullmannite structure, which retains the cubic cell. However, the symmetry is lowered from $P2_1/a\bar{3}$ to $P2_13$. Another possibility for an ordered arrangement of the anions is the cobaltite (CoAsS) type structure. This structure has orthorhombic symmetry $Pca2_1$; however, the lattice constants a , b , and c are very similar and accidentally might even be the same. Thus, the X-ray powder patterns of compounds with pyrite, ullmannite, and cobaltite type structures may all look alike. A comparison of the positional parameters as obtained for pyrite, FeS_2 (15), ullmannite, NiSbS (6), and cobaltite, CoAsS (16) is given in Table 2.

The precession diagrams of all eight pyrite-related compounds showed no superstructure reflections, thus

confirming the cubic or pseudocubic translational symmetry. Intensity data for these crystals were recorded on a four-circle Enraf-Nonius (CAD4) diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation and a scintillation counter with pulse-height discrimination. The scans were along the Laue streaks ($\theta/2\theta$) with background scans at both sides of each reflection. Absorption corrections were made on the basis of ψ scan data. The structures were refined with a full-matrix least-squares program taken from the program package SHELX-97 (17) using atomic scattering factors, corrected for anomalous dispersion, as provided by the program. The weighting scheme accounted for the counting statistics and a parameter correcting for secondary

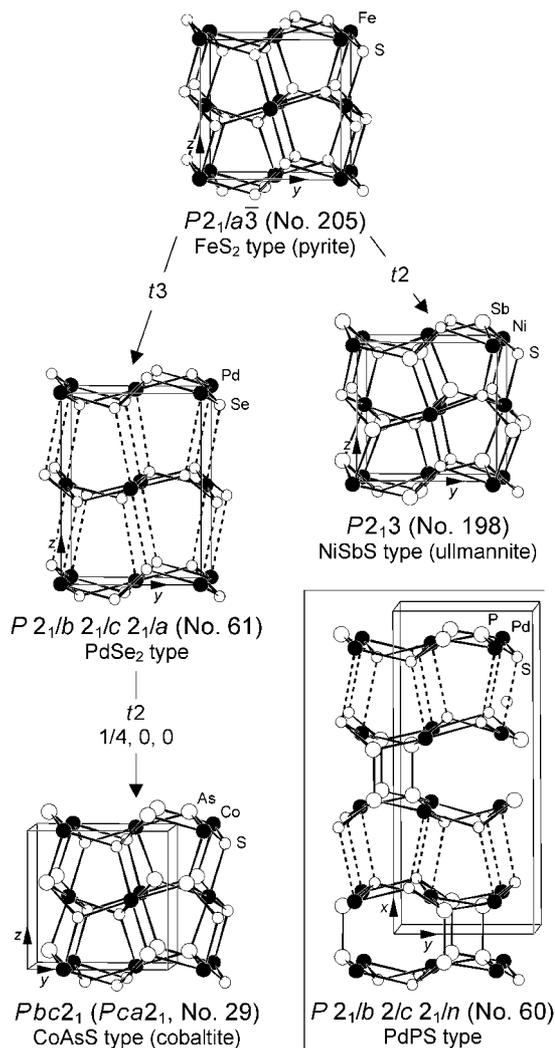


FIG. 2. Symmetry relations for some pyrite-related compounds. The space groups of the structures of PdSe_2 , CoAsS , and NiSbS are all *translationengleiche* (t) subgroups of the cubic space group of pyrite. The structure of PdPS is shown here only for comparison. It may be considered as a stacking variant of the ullmannite structure. Its space group is not a subgroup of the space group of ullmannite.

TABLE 2
Comparison of the Positional Parameters of Pyrite (FeS₂),
Ullmannite (NiSbS), and Cobaltite (CoAsS)^a

		<i>x</i>	<i>y</i>	<i>z</i>
FeS ₂	<i>Pa</i> 3 (No. 205)			
Fe	4 <i>a</i>	0	0	0
S	8 <i>c</i>	0.384	0.384	0.384
NiSbS	<i>P2</i> ₁ 3 (No. 198)			
Ni	4 <i>a</i>	0.976	0.976	0.976
Sb	4 <i>a</i>	0.625	0.625	0.625
S	4 <i>a</i>	0.390	0.390	0.390
CoAsS	<i>Pbc</i> 2 ₁ (No. 29)			
Co	4 <i>a</i>	0.260	0.995	0
As	4 <i>a</i>	0.869	0.619	0.617
S	4 <i>a</i>	0.631	0.384	0.381

^aTo facilitate comparisons the positional parameters of the cobaltite structure are listed in the nonstandard setting *Pbc*2₁. With respect to the pyrite and ullmannite type structures the origin of the cobaltite type structure is shifted by $\Delta x = \frac{1}{4}$.

extinction was optimized as a least-squares variable. Additional crystallographic data and some results are summarized in Table 3.

The distinction between the three possible structure types—pyrite, ullmannite, and cobaltite—was clearly possible for NiAsS, NiSbS, PdAsS, PdAsSe, PdSbSe, and PdSbTe. For these six compounds the lowest residuals were obtained for the ullmannite type structure. The possibility to distinguish the three structures is no surprise for the four compounds NiAsS, NiSbS, PdAsS, and PdSbSe, since in these compounds the scattering powers of the pnictogen and chalcogen atoms differ greatly. For PdAsSe and PdSbTe the scattering powers of the main group elements differ only by one electron. Nevertheless, the atomic order of these elements could be established, because the positional parameters *x* of the palladium atoms obtained during the structure refinements differ significantly from zero, the value fixed by symmetry in the pyrite type structure. Also, the distinction between the ullmannite and the cobaltite type structure was clearly possible for these two compounds because of the difference in the space group extinctions, as was already observed on the precession diagrams, and confirmed during the structure refinements. In contrast, the three structure types could not be clearly distinguished for the compounds NiPS and NiAsSe. For these two compounds the positions of the nickel atoms are too close to the origin of the unit cell and the positional parameters of the other atoms are also very similar to those of pyrite. Here we simply have to assume that the ullmannite structure is correct by analogy, since this is the atomic order found for the other homologous compositions. The results of the structure refinements are listed in Tables 3–5.

(ii) *NiP*_{1.86}*Se*_{0.14}, *NiP*_{0.24}*Se*_{1.76}, and *NiSbSe*

The sample with the nominal composition NiPSe contained two phases which turned out to be the end members of solid solutions of the binary phase NiP₂, prepared at high pressure (18), and NiSe₂ (19), both with pyrite type structure. The crystal structures of these solid solutions were refined from X-ray powder diffractometer data, resulting in the compositions NiP_{1.86(4)}Se_{0.14(4)} and NiP_{0.24(4)}Se_{1.76(4)}. The sample of NiSbSe was obtained only in microcrystalline form. Its ullmannite type structure was also refined from powder data. The samples of these compounds were ground to fine powders and placed between acetate foils. The intensity data were recorded from rotating samples on a focussing powder diffractometer (STOE Stadi P) with monochromated CuK α ₁ radiation, using a linear position-sensitive detector in transmission geometry. The structures were refined with the Rietveld method using the program FULLPROF (20). During each refinement a scale factor, the lattice constant *a*, four parameters to fit the peak profiles with a pseudo-Voigt function, and one parameter for the zero point of the diffractogram were optimized. All atoms were refined with isotropic thermal parameters. Further details of the data collections and the structure refinements are summarized in Table 6. The quality of the refinements may be judged from the Rietveld plots shown in Fig. 3. The atomic parameters and interatomic distances of all powder refinements are listed in Tables 4, 5, 7, and 8.

(iii) *Ni*_{0.77}*Sb*_{0.5}*Te*_{0.5} and *PdPSe*

Our sample corresponding to the nominal composition NiSbTe contained as the major reaction product a NiAs type phase. Its lattice constants are listed in Table 1. They differ considerably from those previously obtained for the solid solution series NiSb_{1-x}Te_x with NiAs type structure (9). This can be rationalized by the different composition of our sample with a nickel to nonmetal ratio of 1:2 as compared to 1:1 in the previous investigation. The energy-dispersive X-ray analysis of our sample in a scanning electron microscope showed as an average for two crystals the Ni:Sb:Te ratio of 77(2):50(3):50(3). This Sb:Te ratio of 50:50 was held constant during the subsequent single-crystal structure refinement, which was carried out as described above. It resulted in an occupancy parameter for the nickel position corresponding to the composition Ni_{0.766(5)}Sb_{0.50}Te_{0.50}. Hence, in our compound 23.4(5)% of the nickel positions were found to be unoccupied, whereas for a solid solution NiSb–NiTe a full occupancy of the nickel position might be assumed. The cell volume of our ternary NiAs sample amounted to 0.06886(3) nm³ as compared to 0.0709 nm³ calculated from the data given in the diagram for the composition NiSb_{0.5}Te_{0.5} in the previous investigation of this solid solution series (9).

TABLE 3
Crystal Data for Transition Metal Pnictide Chalcogenides Refined from Single-Crystal Data^{a,b}

Formula	NiPS	NiAsS	NiSbS	NiAsSe	Ni _{0.77} Sb _{0.5} Te _{0.5}	PdAsS	PdPSe	PdAsSe	PdSbSe	PdSbTe
Structure type	NiSbS	NiSbS	NiSbS	NiSbS	NiAs	NiSbS	PdPS	NiSbS	NiSbS	NiSbS
Space group	<i>P</i> 2 ₁ 3 (No. 198)	<i>P</i> 6 ₃ / <i>mmc</i> (No. 194)	<i>P</i> 2 ₁ 3 (No. 198)	<i>P</i> bcn (No. 60)	<i>P</i> 2 ₁ 3 (No. 198)	<i>P</i> 2 ₁ 3 (No. 198)	<i>P</i> 2 ₁ 3 (No. 198)			
Lattice constants ^b										
<i>a</i> (pm)	553.86(7)	568.88(9)	593.41(7)	584.69(9)	391.58(4)	595.07(7)	1359.4(4)	609.48(5)	632.40(6)	653.62(6)
<i>b</i> (pm)	—	—	—	—	—	—	1583.17(8)	—	—	—
<i>c</i> (pm)	—	—	—	—	520.11(7)	—	1585.83(7)	—	—	—
Cell volume (nm ³)	0.16990(4)	0.18410(5)	0.20896(5)	0.19988(5)	0.06907(1)	0.21072(4)	0.4644(2)	0.22640(4)	0.25292(5)	0.27924(5)
Formula units/cell	4	4	4	4	1	4	8	4	4	4
Formula mass	121.73	165.68	212.51	215.57	169.63	213.41	216.35	260.30	307.13	355.77
Calcd density (g/cm ³)	4.80	5.98	6.75	7.07	8.18	6.74	6.19	7.64	8.08	8.48
Crystal size (μm)	75 × 80 × 130	35 × 55 × 50	30 × 30 × 80	25 × 25 × 25	40 × 50 × 10	10 × 25 × 50	2 × 10 × 60	50 × 60 × 90	75 × 95 × 125	75 × 90 × 100
Scans up to 2θ (°)	90	70	70	70	70	70	65	70	70	60
Range in <i>h</i>	± 11	± 9	± 9	± 9	± 6	± 9	± 20	± 9	− 8 ≤ <i>h</i> ≤ 10	± 9
<i>k</i>	± 11	± 9	± 9	± 9	± 6	± 9	± 8	± 9	− 8 ≤ <i>k</i> ≤ 10	± 9
<i>l</i>	− 11 ≤ <i>l</i> ≤ 9	± 9	± 9	− 9 ≤ <i>l</i> ≤ 8	± 8	− 9 ≤ <i>l</i> ≤ 8	± 8	± 9	− 8 ≤ <i>l</i> ≤ 10	± 9
Max./min. transmission	1.58	1.08	2.38	1.44	1.54	1.51	1.20	1.62	1.32	1.36
Total no. of reflections	5420	3300	3742	3173	1240	4050	6703	4548	3249	3238
Unique reflections	469	276	318	292	78	318	842	332	373	276
Internal residual (<i>I</i>)	0.058	0.102	0.040	0.100	0.054	0.101	0.204	0.051	0.058	0.108
Reflns with <i>I</i> ₀ > 2σ(<i>I</i> ₀)	338	207	312	145	70	230	458	311	309	270
No. of variables	12	12	12	12	7	12	29	12	12	12
Convent. residual (<i>F</i> > 2σ)	0.014	0.026	0.009	0.016	0.016	0.024	0.035	0.012	0.015	0.028
Weighted residual (all <i>F</i> ²)	0.033	0.059	0.021	0.040	0.032	0.045	0.092	0.025	0.028	0.057
Flack parameter	0.36(38)	0.45(5)	0.00(3)	0.13(31)	—	0.00(3)	—	0.49(4)	0.00(3)	0.35(53)
Diff. electr. dens. max. (e/Å ³)min.	− 0.57 − 0.62	− 1.66 − 1.55	− 0.45 − 0.48	− 2.20 − 1.71	− 0.86 − 1.51	− 2.35 − 2.38	− 1.98 − 1.89	− 0.62 − 0.54	− 1.31 − 1.27	− 2.12 − 2.11

^aStandard deviations in the place values of the last listed digits are given in parentheses throughout the paper.

^bThese lattice constants were obtained from the data recorded on the single-crystal diffractometer.

TABLE 4
Atomic Parameters of Ullmannite (NiSbS) Type Compounds^a

Compound	Atom	Occupancy (%)	$x = y = z$	$U_{11} = U_{22} = U_{33}$ (pm ²)	$U_{12} = U_{13} = U_{23}$ (pm ²)	U_{eq} (pm ²)
NiPS	Ni	100.0(2)	0.0000(2)	51.6(5)	0.2(3)	51.6(5)
	P	99.8(3)	0.6118(4)	48(6)	2(4)	48(6)
	S	100.0(3)	0.3882(4)	71(6)	3(4)	71(6)
NiAsS	Ni	98.5(8)	0.9944(2)	47(2)	2(3)	47(2)
	As	97.8(9)	0.6182(1)	68(3)	2(4)	68(3)
	S	100.0(8)	0.3849(3)	13(3)	1(7)	13(3)
NiSbS	Ni	99.9(2)	0.98123(4)	65.5(8)	0.2(7)	65.5(8)
	Sb	100.0(1)	0.62674(2)	65.2(6)	3.5(4)	65.2(6)
	S	99.7(3)	0.38118(7)	70(1)	-1(1)	70(1)
NiAsSe	Ni	100.0(3)	0.0001(8)	60(2)	3(2)	60(2)
	As	100.0(6)	0.6208(6)	53(8)	7(10)	53(8)
	Se	99.6(6)	0.3789(6)	69(8)	6(10)	69(8)
NiSbSe (powder refinement)	Ni	100.0(6)	0.9871(7)	—	—	78(15)
	Sb	99.4(6)	0.6278(5)	—	—	103(8)
	Se	98.8(9)	0.3784(6)	—	—	204(16)
PdAsS	Pd	99.5(3)	0.9997(1)	61(1)	0(1)	61(1)
	As	100.0(3)	0.6129(1)	73(2)	1(4)	73(2)
	S	98.9(7)	0.3919(3)	61(4)	10(10)	61(4)
PdAsSe	Pd	99.3(3)	0.99390(4)	67.8(8)	-0.6(5)	67.8(8)
	As	100.0(3)	0.61403(5)	61(1)	5(1)	61(1)
	Se	98.8(4)	0.38380(5)	87(1)	8(1)	87(1)
PdSbSe	Pd	99.8(1)	0.99618(4)	76.6(9)	-1.5(8)	76.6(9)
	Sb	99.8(2)	0.62342(3)	84(1)	7(1)	84(1)
	Se	100.0(2)	0.38203(5)	87(1)	6(1)	87(1)
PdSbTe	Pd	99.9(3)	0.99802(9)	91(3)	0(2)	91(3)
	Sb	100.0(3)	0.62709(7)	97(3)	12(2)	97(3)
	Te	99.8(6)	0.37278(7)	114(3)	10(2)	114(3)

^a All atoms occupy the position $4a$ (x, x, x) of space group $P2_13$. The listed occupancy parameters had been obtained in previous least-squares cycles. In the final refinements the ideal occupancy parameters were used.

Our single-crystal investigation of the palladium phosphide selenide PdPSe confirmed the PdPS type structure found for that compound from X-ray powder data (7, 8).

The results of the structure refinements of Ni_{0.766(5)}Sb_{0.5}Te_{0.5} and PdPSe are summarized in the Tables 3 and 8–11.

TABLE 5
Interatomic Distances in Ullmannite (NiSbS) Type Compounds^a

Compound	$T-Pn$	pm	$T-Ch$	pm	$Pn-Ch$	pm
NiPS	Ni-P	231.5(1)	Ni-S	231.5(1)	P-S	213.89(6)
NiAsS	Ni-As	240.0(1)	Ni-S	234.8(1)	As-S	229.9(2)
NiSbS	Ni-Sb	256.28(4)	Ni-S	237.56(4)	Sb-S	252.37(8)
NiAsSe	Ni-As	243.1(6)	Ni-Se	243.1(6)	As-Se	244.9(1)
NiSbSe	Ni-Sb	259.2(6)	Ni-Se	246.2(7)	Sb-Se	263.0(5)
PdAsS	Pd-As	249.21(7)	Pd-S	250.0(1)	As-S	227.6(3)
PdAsSe	Pd-As	258.41(3)	Pd-Se	251.09(3)	As-Se	243.03(6)
PdSbSe	Pd-Sb	264.66(3)	Pd-Se	261.39(3)	Sb-Se	264.36(6)
PdSbTe	Pd-Sb	271.51(6)	Pd-Te	269.15(6)	Sb-Te	287.7(1)

^a The transition metal atoms ($T = \text{Ni, Pd}$) are coordinated by three pnictogen ($Pn = \text{P, As, Sb}$) and three chalcogen ($Ch = \text{S, Se, Te}$) atoms in distorted octahedral coordination (site symmetry 3). The Pn and Ch atoms form $Pn-Ch$ pairs. With three additional T neighbors they obtain distorted tetrahedral coordination, again with site symmetry 3. The distances were calculated using the lattice constants as obtained from the Guinier powder data (Table 1).

DISCUSSION

We have investigated samples for all 18 combinations with the compositions $TPnCh$ ($T = \text{Ni, Pd}$; $Pn = \text{P, As, Sb}$; $Ch = \text{S, Se, Te}$). In previous investigations the atomic order of the main-group elements had been established only for the mineral ullmannite (6) with the ideal composition NiSbS. The lattice constants (Table 1) reported for the mineral are different from those of synthetic samples because of varying amounts of other elements present in the mineral, notably cobalt and arsenic. We now have clearly established the ullmannite type structure for NiAsS, NiSbS, NiSbSe, PdAsS, and PdSbSe on the basis of the differing scattering power of the pnictogen and chalcogen components. The same atomic order as in ullmannite was found by us also for the compounds PdAsSe and PdSbTe as a result of the positional parameters of the metal atoms, which cause the Pd-As (258.4 pm) and Pd-Sb distances (271.5 pm) to be

TABLE 6
Crystallographic Data for $\text{NiP}_{1.86(4)}\text{Se}_{0.14(4)}$, $\text{NiP}_{0.24(4)}\text{Se}_{1.76(4)}$, and NiSbSe^a

Formula	$\text{NiP}_{1.86(4)}\text{Se}_{0.14(4)}$	$\text{NiP}_{0.24(4)}\text{Se}_{1.76(4)}$	NiSbSe
Structure type	Pyrite	Pyrite	NiSbS
Space group	$Pa\bar{3}$ (No. 205)	$Pa\bar{3}$ (No. 205)	$P2_13$ (No. 198)
Lattice constant a (pm)	547.9(1)	590.1(1)	608.68(6)
Cell volume (nm^3)	0.1645	0.2055	0.2255
Formula units/cell	4	4	4
Formula mass	127.36	205.09	259.40
Theoretical density (g/cm^3)	5.146	6.620	7.635
Range in 2θ ($^\circ$)	20–90	20–90	10–90
Step width in 2θ ($^\circ$)	0.02	0.02	0.02
Total measuring time (h)	7	7	13
Total number of steps	3500	3500	4000
Number of reflections	23	30	43
Total number of variables	17	17	13
Number of structural parameters	14	14	16
Goodness of fit (χ^2)	4.78	4.78	1.47
Bragg residual R_{Bragg}	2.45	5.19	0.848
Conventional residual R_F	5.50	3.93	1.15

^aThe Rietveld refinements of $\text{NiP}_{1.86(4)}\text{Se}_{0.14(4)}$ and $\text{NiP}_{0.24(4)}\text{Se}_{1.76(4)}$ were carried out by a simultaneous refinement of both structures from one X-ray powder diffractometer spectrum. Lattice constants are taken from refinements of Guinier powder data.

different from those of Pd–Se (251.1 pm) and Pd–Te (269.2 pm), respectively. Only for NiPS, NiAsSe, and PdSbS the atomic order could not be established experimentally. For the two compounds NiPS and NiAsSe with very similar scattering power of the main-group elements the positional parameters of the nickel atoms differ too little from zero, the value fixed by symmetry in the pyrite type structure. In the case of PdSbS our powder sample did not have the purity required for an accurate structure refinement.

As already mentioned above, the space group symmetries of the ullmannite and cobaltite type structures are lower than the symmetry of the pyrite type structure. Since the positional parameters of these three structures are very similar, one has to be aware that crystals of the compounds with (the lower symmetry) ullmannite and cobaltite structures might be twinned. The symmetry elements lost on going from the higher symmetric to the lower symmetric structure (Fig. 2) can be expected to occur as twin elements. In the case of the ullmannite type structure (space group $P2_13$) the center of symmetry present in the pyrite type structure (space group $Pa\bar{3}$) is lost. Hence, we can expect inversion twins. We have refined from the single-crystal data the volume ratios of these expected twin domains for all compounds with the ullmannite structure. These ratios are listed in Table 3 in the form of the Flack parameter (21). For

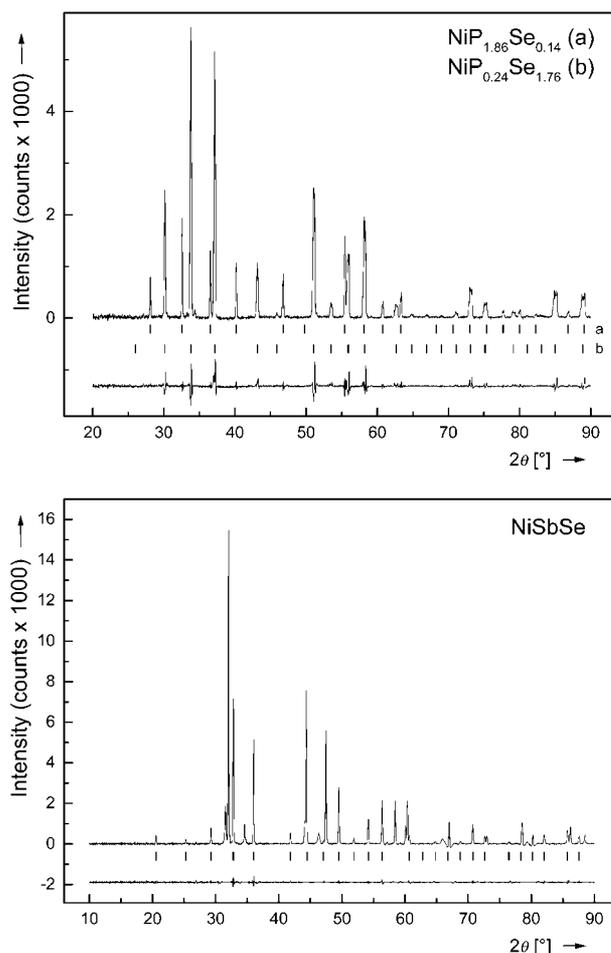


FIG. 3. Rietveld refinement plots for $\text{NiP}_{1.86(4)}\text{Se}_{0.14(4)}$, $\text{NiP}_{0.24(4)}\text{Se}_{1.76(4)}$, and NiSbTe . The peak positions and the difference profiles between the calculated and the observed plots are shown in the lower part of each diffractogram.

the crystals of NiSbS, PdAsS, and PdSbSe we obtained a Flack parameter of zero, indicating single-domain crystals of this acentric structure. For the other five crystals the Flack parameters showed values between 0.13(31) and 0.49(4) (albeit for some with very large standard deviations),

TABLE 7
Atomic Parameters of the Pyrite Type Solid Solutions $\text{NiP}_{1.86}\text{Se}_{0.14}$ and $\text{NiP}_{0.24}\text{Se}_{1.76}^a$

Compound	Atom	$Pa\bar{3}$	Occupancy		B $x = y = z$ (10^4 pm^2)
			(%)		
$\text{NiP}_{1.86(4)}\text{Se}_{0.14(4)}$	Ni	$4a$	100	0	0.9(2)
	P/Se	$8c$	193(2)/7	0.3839(5)	0.8(2)
$\text{NiP}_{0.24(4)}\text{Se}_{1.76(4)}$	Ni	$4a$	100	0	0.8(1)
	P/Se	$8c$	112(2)/88	0.3844(2)	0.46(6)

^aParameters which were constrained are given without standard deviations.

TABLE 8
Interatomic Distances in Pyrite and NiAs Type Compounds^a

NiP _{1.86(4)} Se _{0.14(4)} pyrite type	NiP _{0.24(4)} Se _{1.76(4)} pyrite type	Ni _{0.766(5)} Sb _{0.50(3)} Te _{0.50(3)} NiAs type
Ni: 6 P/Se 228.8(3)	Ni: 6 P/Se 246.6(1)	Ni: 6 Sb/Te 260.52(5)
P/Se: 1 P/Se 220.4(4)	P/Se: 1 P/Se 236.4(2)	2 Ni 259.70(5)
3 Ni 228.8(3)	3 Ni 246.6(1)	Sb/Te: 6 Ni 260.52(5)

^a The distances (pm) were calculated using the lattice constants as obtained from the Guinier powder data.

indicating inversion twins. In this context, we should mention that we expect equal amounts of right- and left-handed crystals in the samples. For that reason we report all results with the same handedness. In the case of the cobaltite type structure the twinning could have mimicked a threefold axis. Thus, the “single” crystal data might very well suggest a higher symmetric cubic structure. However, as already mentioned above, we could rule out the cobaltite type structure for all compounds listed in Table 4—with NiPS, NiAsSe, and PdSbS as the only exceptions—on the basis of the differences in the space group extinctions.

In the sample with the nominal composition “NiPSe” we observed the end-members of solid solutions NiP_{1.86(4)}Se_{0.14(4)} and NiP_{0.24(4)}Se_{1.76(4)} derived from the binary pyrite type compounds NiP₂, prepared at high pressure (18), and NiSe₂ (19). In this context it may be of interest to know that pyrite type “NiP₂” can be prepared at normal pressure from a lithium flux. The structure refinement from single-crystal data did not reveal any lithium content (22) However, only a small amount of interstitial lithium may be required to stabilize pyrite-type “NiP₂.” The additional electrons coming from the interstitial lithium atoms would increase the electron count of the band structure in a way similar to that of pyrite type NiP_{1.86(4)}Se_{0.14(4)} found during the present investigation.

For the sample with the composition “NiSbTe” we obtained a ternary defect-NiAs type compound with the composition Ni_{0.766(5)}Sb_{0.50(3)}Te_{0.50(3)}. Both corresponding binary compounds NiSb (23) and NiTe (24) have been reported with NiAs type structures. Both of these binary

TABLE 9
Atomic Parameters of the NiAs Type Compound
Ni_{0.766(5)}Sb_{0.50(3)}Te_{0.50(3)}^a

Atom	<i>P</i> 6 ₃ / <i>mmc</i>	Occupancy (%)	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (pm ²)
Ni	2 <i>a</i>	76.6(5)	0	0	0	88(4)
Sb/Te	2 <i>c</i>	50(3)/50 ^a	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	92(2)

^a The ratio of Sb:Te was determined by EDX analyses.

compounds are also reported to form extended defect-NiAs type solid solutions with the compositions Ni_{0.88(1)}Sb (23) and Ni_{0.50(1)}Te (24) as end-members. The composition Ni_{0.766(5)}Sb_{0.50(3)}Te_{0.50(3)} found by us for the ternary compound is close to the average composition Ni_{0.69}Sb_{0.50}Te_{0.50} of the binary defect-NiAs type compounds. The samples prepared to obtain the “missing” members NiPTe, NiAsTe, PdPTe, and PdAsTe contained known binary compounds. The ternary compounds remain elusive.

The crystal structure of PdPSe presently refined from single-crystal X-ray data confirms the PdPS structure, previously assigned on the basis of X-ray powder data (8). Again, the largest thermal parameters (Table 10) are those which result in the largest displacements in the *x* direction, the direction which is perpendicular to the sheets of this layered structure (Fig. 2). The Pd–P distances in the selenide are slightly longer than in the sulfide (averages of 230.5(3) pm vs 229.0(2) pm). This is also the case for the shortest Pd–Pd distances (321.2(1) pm vs. 319.8(1) pm). However, the P–P distances in the center of the *Ch*–P–P–*Ch* chain are shorter in the selenium compound (218.9(4) pm) than in PdPS (220.6(2) pm). This may be rationalized by the relatively high electronegativity of the sulfur atoms (as compared to that of selenium) which withdraws electron density from the P–P bond. As might be expected, the interatomic distances involving the selenium atoms are all longer by between 6 pm (for the weak Pd–*Ch* interactions) and 16 pm (for the P–*Ch* bonds) when compared to the corresponding distances in the sulfide.

TABLE 10
Atomic Parameters of the PdPS Type Compound PdPSe

Atom	<i>Pbcn</i>	Occupancy ^a (%)	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁ (pm ²)	<i>U</i> ₂₂ (pm ²)	<i>U</i> ₃₃ (pm ²)	<i>U</i> ₁₂ (pm ²)	<i>U</i> ₁₃ (pm ²)	<i>U</i> ₂₃ (pm ²)	<i>U</i> _{eq} (pm ²)
Pd	8 <i>d</i>	199.8(3)	0.38939(6)	0.2410(1)	0.1538(1)	139(3)	52(3)	44(3)	14(3)	7(3)	−2(3)	78(2)
P	8 <i>d</i>	199.0(8)	0.0791(2)	0.3757(5)	0.2850(4)	111(13)	68(11)	63(11)	−4(10)	1(9)	−4(10)	81(5)
Se	8 <i>d</i>	100.0(3)	0.15643(8)	0.1342(2)	0.0389(2)	126(5)	57(4)	54(4)	17(5)	2(4)	−0(4)	79(2)

^a These occupancy parameters were obtained in a separate series of least-squares refinements. The atomic parameters listed in this table resulted from a refinement with ideal occupancy values.

TABLE 11
Interatomic Distances in PdPSe^a

Pd: 1 P	230.5(3)	P: 1 P	218.9(4)	Se: 1 P	227.3(3)
1 P	230.5(2)	1 Se	227.3(3)	1 Pd	245.1(1)0
1 Se	245.1(1)	1 Pd	230.5(3)	1 Pd	247.0(1)
1 Pd	247.0(1)	1 Pd	230.5(2)	1 Pd	329.7(2)
1 Pd	321.2(1)				
1 Se	329.7(2)				

^aThe distances (pm) were calculated using the lattice constants as obtained from the Guinier powder data.

Chemical bonding and the physical properties of the compounds with the ullmannite structure as well as PdPS and PdPSe can be rationalized on the basis of the classical concept of the two-electron bond (25–30, and references therein). With this concept two electrons are counted for each of the *T–Pn*, *T–Ch*, and *Pn–Ch* bonds. Using oxidation numbers (formal charges), where the electrons of the more or less covalent bonds are counted at the anionic components, one arrives for the ullmannite type compounds with NiPS as example at the formula $\text{Ni}^{3+}[\text{P–S}]^{-3}$. This electron count follows the octet rule for the phosphorus and sulfur atoms. For the nickel atoms one obtains a “d⁷ system,” i.e., the nickel atoms have 19 electrons. Of these, 12 electrons are located in the three Ni–P and three Ni–S bonds (these bonding electrons are counted twice, not only at the nickel atoms, but also at the pnictogen and chalcogen atoms to complete the octets of these main-group elements). Six electrons use nonbonding orbitals of the nickel atoms, thus increasing the electron count at the nickel atoms to 18. And the 19th electron of the nickel atoms is delocalized in the (antibonding) conduction band. Consequently, metallic conductivity has been found for NiPS (12) and NiAsS (5), and this can also be assumed for the other isoelectronic nickel and palladium pnictide chalcogenites with ullmannite type structure. The closely related compound CoAsS with cobaltite type structure has the same near-neighbor coordinations as ullmannite type NiPS and NiAsS (Fig. 2). In analogy, this compound can be rationalized with the formula $\text{Co}^{3+}[\text{As–S}]^{3-}$. Thus, the cobalt atoms obtain a “d⁶ system,” and in counting two electrons for each of the localized three Co–As and three Co–S bonds they follow the 18-electron rule. Consequently, the conduction band is empty, and CoAsS is semiconducting (5, 31).

Chemical bonding in PdPS has been discussed on the basis of the two-electron bond (8) and using extended Hückel calculations (32). In addition to the classical two-electron bonds, the structure contains a weakly bonding interaction between—in terms of the classical terminology—the lone pair of the sulfur atoms and the filled “non-bonding” d_{z²} orbital of the palladium atoms with a bond length of 323.1(2) pm. This bond is drawn with dashed

lines in Fig. 2 and amounts to 329.7(2) pm in the corresponding selenium compound PdPSe as found during the present investigation. Unfortunately, this weakly bonding interaction has not been discussed by Burdett and Coddens (32).

Simple algebraic formulas have been developed to rationalize chemical bonding on the basis of the two-electron bond in semiconductors. Using these formulas Parthé had predicted the near-neighbor environments in the then unknown crystal structures of semiconducting PdPS and PdPSe (33) which subsequently were confirmed by the structure determination of PdPS (8). It is the predictive character of this simple model of the two-electron bond which makes it so useful for the rationalization of chemical bonding in such compounds.

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REFERENCES

1. R. A. Yund, *Am. J. Sci.* **260**, 761 (1962).
2. F. Hulliger, *Nature* **198**, 382 (1963).
3. D. D. Klemm, *Neues Jahrb. Mineral. Abh.* **103**, 205 (1965).
4. M. El-Boragy and K. Schubert, *Z. Metallkd.* **62**, 667 (1971).
5. J. J. Steger, H. Nahigian, R. J. Arnott, and A. Wold, *J. Solid State Chem.* **11**, 53 (1974).
6. Y. Takéuchi, *Miner. J. Jap.* **2**, 90 (1957).
7. T. A. Bither, P. C. Donohue, and H. S. Young, *J. Solid State Chem.* **3**, 300 (1971).
8. W. Jeitschko, *Acta Crystallogr. B* **30**, 2565 (1974).
9. G. I. Makovetskii and G. M. Shakhlevich, *Inorg. Mater.* **18**, 186 (1982); translation of *Izv. Akad. Nauk. SSSR, Neorg. Mater.* **18**, 226 (1981).
10. D. J. Braun and W. Jeitschko, *J. Solid State Chem.* **32**, 357 (1980).
11. K. Yvon, W. Jeitschko, and E. Parthé, *J. Appl. Crystallogr.* **10**, 73 (1977).
12. R. Henry, H. Nahigian, J. Steger, and A. Wold, *Inorg. Chem.* **14**, 2912 (1975).
13. P. Bayliss, *Am. Mineral.* **62**, 369 (1977).
14. J. L. Pratt and P. Bayliss, *Am. Mineral.* **65**, 154 (1980).
15. G. Brostigen and A. Kjekshus, *Acta Chem. Scand.* **23**, 2186 (1969).
16. P. Bayliss, *Am. Mineral.* **67**, 1048 (1982).
17. G. M. Sheldrick, *SHELX-97*, A Program System for the Determination and Refinement of Crystal Structures, Universität Göttingen, 1997.
18. P. C. Donohue, T. A. Bither, and H. S. Young, *Inorg. Chem.* **7**, 998 (1968).
19. F. Grønvald and E. Jacobsen, *Acta Chem. Scand.* **10**, 1440 (1956).
20. J. Rodriguez-Carvajal, FULLPROF, version 2.6.1, Oct. 94, ILL (unpublished), based on the original code provided by D. B. Wiles and A. Sakthivel, *J. Appl. Crystallogr.* **14**, 149 (1981).

21. H. D. Flack, *Acta Crystallogr. A* **39**, 876 (1983).
22. D. Paschke and W. Jeitschko, unpublished results, 1992.
23. A. Kjekshus and K. P. Walseth, *Acta Chem. Scand.* **23**, 2621 (1969).
24. J. Barstad, F. Grønvold, E. Røst, and E. Vestersjø, *Acta Chem. Scand.* **20**, 2865 (1966).
25. E. Mooser and W. B. Pearson, *Progress Semicond.* **5**, 103 (1960).
26. F. Hulliger, *Struct. Bonding* **4**, 83 (1968).
27. A. Kjekshus and T. Rakke, *Struct. Bonding* **19**, 45 (1974).
28. M. H. Möller and W. Jeitschko, *Inorg. Chem.* **20**, 828 (1981).
29. R. Rühl and W. Jeitschko, *Inorg. Chem.* **21**, 1886 (1982).
30. W. Jeitschko, U. Flörke, M. H. Möller, and R. Rühl, *Ann. Chim. (Paris)* **7**, 525 (1982).
31. F. Hulliger and E. Mooser, *J. Phys. Chem. Solids* **26**, 429 (1965).
32. J. K. Burdett and B. A. Coddens, *Inorg. Chem.* **27**, 418 (1988).
33. E. Parthé, *Acta Crystallogr. B* **29**, 2808 (1973).